

Molecular Vibrational Response of Ice Layers after Ultrashort-Laser Excitation of Metal Surfaces

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Abstract: Electron injection into thin, crystalline D₂O layers on a Ru(001) surface after UV excitation has been investigated using broadband sum-frequency generation spectroscopy, whereby a signal enhancement by several orders of magnitude is observed.

1. Introduction

Electrons as excess charges in polar solvents result in molecular motion within the solvent to stabilize the new charge distribution known as electron solvation [1]. We employ time-resolved broadband-IR-VIS SFG (sum frequency generation) spectroscopy as a powerful technique to study the changes in the vibrational spectra of D₂O water layers upon electron injection from a Ru(001) surface. Unlike in time-resolved photoemission experiments where the electron binding energy is traced and the solvent response are inferred subsequently [2,3], SFG vibrational spectroscopy *directly* monitors the molecular reorientation induced by the excess charge.

2. Experiment

The experiments were carried out in an ultrahigh vacuum chamber (base pressure $1 \cdot 10^{-10}$ mbar) equipped with standard surface science tools. A commercial Ti:sapphire laser has been employed whose output is centered at 800 nm with pulses of around 100 fs in duration and 4.5 mJ in pulse energy at a repetition rate of 400 Hz. Less than one third of the fundamental output is frequency tripled to provide UV light at 266 nm (4.65 eV) with 15 μ J per pulse. The remaining part is used to pump an optical parametric generator/amplifier, providing tunable IR pulses in the region between 2 to 10 μ m at a bandwidth of ~ 150 cm^{-1} with typical pulse durations and energies of 150 fs and 15 μ J, respectively. While working in the spectral range of CO₂ and H₂O absorption, the beam path is continuously purged with nitrogen, enabling us to measure the SFG signal without any detectable IR-intensity loss due to the ambient air. Crystalline ice layers are grown in ultrahigh vacuum by dosing of D₂O at rates lower than 2BL/min through a pinhole doser onto a Ru(001) single-crystal surface at 155 K which is subsequently annealed to 160 K for ~ 1 s. The actual water coverage is determined from thermal desorption spectra (TDS) taken after each SFG experiment. Amorphous ice was prepared by dosing water onto the cold Ru(001) crystal (below 50 K) [4] and at higher rates.

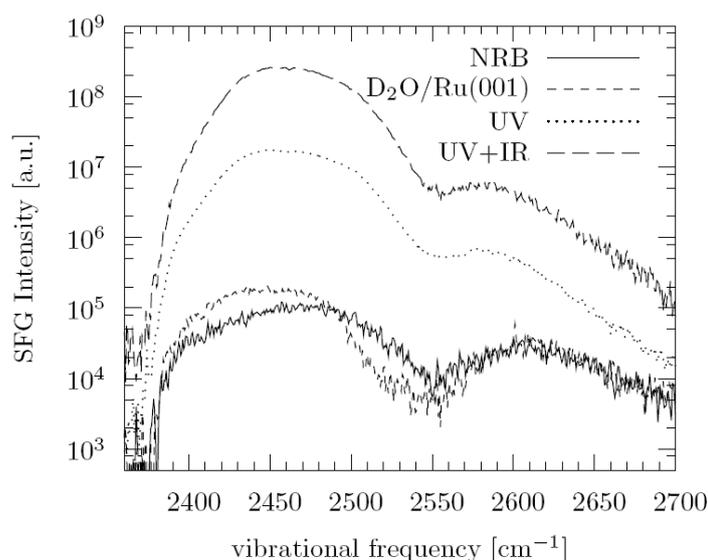


Fig. 1. Raw SFG spectra of 8 BL crystalline D₂O on Ru(001) (half-dashed; D₂O/Ru(001)). Intensity of the IR pulse is shown as non-resonant SFG signal from the sample surface (solid; NRB). Upon irradiation with 4.65 eV, the peak phase shifts and the amplitude increases by a factor of $\sim 10^3$ (points; UV). If UV and IR pulse temporally overlap, a further signal increase is observed (dashed; UV+IR).

3. Results and discussion

When the ruthenium surface is excited with 266-nm (4.65 eV) photons, excess electrons injected into the adsorbate layer induce –dependent on layer morphology and layer thickness– drastic changes in the vibrational spectra of the OD stretch vibration. While in amorphous ice layers only weak changes are observed, a SFG signal increase by several orders of magnitude is found in crystalline D₂O layers (enhancement factor of 10³ up to 10⁴). Typical raw SFG spectra of crystalline ice/Ru(001) are shown in Fig. 1. The difference between the SFG signal from a bare and a ice covered surface in the region shown arises mainly from the vibrational bands of the O-D stretch oscillations within crystalline ice/Ru(001) located at ~2730 cm⁻¹, ~2480 cm⁻¹ and ~2280 cm⁻¹ (free, half and fully coordinated D₂O species) [5,6]. As can be seen in Fig. 2, the relative SFG enhancement caused by confined excess electrons exhibits spectrally distinct features with even a signal attenuation above 3000 cm⁻¹.

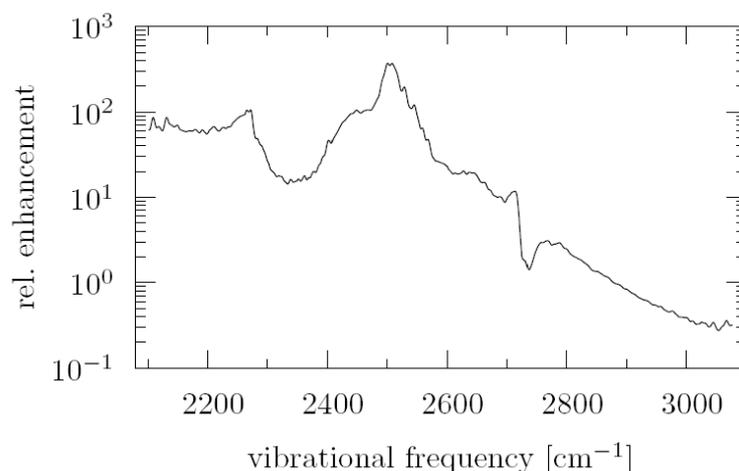


Fig. 2. SFG signal enhancement factor comparing the D₂O covered sample before and after ~20 min irradiation with 4.65 eV light.

Furthermore, coverage and fluence dependent measurements have been performed [6]. The coverage dependent data show a saturation of the signal enhancement at around 10 to 12 BL layer thickness which indicates that the observed SFG signal cannot be dominated from OD oscillators at the water-vacuum interface. Finally, a delay dependence between the UV pump and the IR probe (as part of the SFG probe technique) is found in the experiment which calls for further studies towards IR mediated (induced) processes within the D₂O layer being currently underway.

In summary, we have investigated the vibrational response of thin D₂O layers on a Ru(001) surface, when excess charges originating from the metal substrate cause the hydrogen-bonded network to undergo physical and chemical changes.

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